

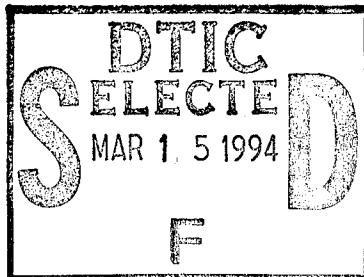
NORTHWESTERN UNIVERSITY

COLLEGE OF ARTS AND SCIENCES
Department of Physics and Astronomy
Technological Institute
2145 No. Sheridan Road
Evanston, IL 60208-3112 USA

Arthur J. Freeman
Morrison Professor of Physics
Tel. (708) 491-3343
Fax. (708) 491-5082
Email. art@freeman.phys.nwu.edu

March 7, 1995

Dr. George Wright
Electronics Division
Office of Naval Research
Department of the Navy
Arlington, VA 22217-5000



Dear George,

Enclosed please find three copies of a final report for my ONR grant titled: *Structural and Electronic Properties of Adsorbates on Semiconductors, Metal-Semiconductor Interfaces and Semiconductor Heterojunctions*, ONR Grant No. N00014-89-J-1290.

Sincerely,

A handwritten signature in black ink, appearing to read "Arthur J. Freeman".
Arthur J. Freeman
Morrison Professor of Physics

jb
Encl.

cc: J. Chiappe, ONR, Chicago ✓
 Defense Tech. Info. Center ✓
 Director, Naval Res. Lab.
 G. Goldberger, ORSP, NU

19950314 030

This document has been approved
for public release and sale; its
distribution is unlimited.

DTIC QUALITY INSPECTED 5

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services Directorate, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	3/7/95	11/1/91 to 10/31/94	
4. TITLE AND SUBTITLE Structural and Electronic Properties of adsorbates on Semiconductors, Metal-Semiconductor Interfaces and Semiconductor Heterojunctions			5. FUNDING NUMBERS
6. AUTHOR(S) A.J. Freeman			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Northwestern University 633 Clark Street Evanston, IL 60208			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Department of the Navy Arlington, VA 22217-5000			10. SPONSORING MONITORING AGENCY REPORT NUMBER N00014-89-J-1290
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Studies of the electronic structure of adsorbates on metal-semiconductor and semiconductor-semiconductor interfaces and semiconductor surfaces were carried out using the molecular cluster LCAO-DVM method (as developed into the DMol program) also in a full potential local (spin) density approach. The new capability of DMol to calculate atomic forces allows automatic geometry optimization and allowed us to study atomic relaxation and reconstruction at the surfaces and interfaces with and without adsorbates. The method calculated variationally self-consistent highly precise solutions of the local density equations with which to determine the structural and electronic properties of the system. Specific problems addressed included studies of: (i) semiconductor heterojunctions (and their bulk constituents) such as Sn/Ge, and (ii) adsorbates on silicon and germanium. The research led to the development of general concepts and simpler theoretical models with which to understand the electronic structure and the relevant parameters governing the interaction between the adsorbate and the substrate. Predictions of theory were compared with experiment. Accurate total energy investigations were undertaken to determine from first principles, equilibrium, internuclear distances, vibrational frequencies, separations and positional (geometric) bonding configurations.			
14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT

FINAL REPORT FOR
ONR Grant No. N00014-89-J-1290

**STRUCTURAL AND ELECTRONIC PROPERTIES OF ADSORBATES ON
SEMICONDUCTORS, METAL-SEMICONDUCTOR INTERFACES
AND SEMICONDUCTOR HETEROJUNCTIONS**

Period of Performance: November 1, 1991 to October 31, 1994

A.J. Freeman, Principal Investigator

I. Background Perspective

An enormous research effort has been concentrated on the metal/silicon interface. Much less work has been done on the metal/Ge interface. In this grant we have concentrated on both Si and Ge as substrate. We present results of extensive studies on both of these in what follows. This will give an indication of the power of the new methods developed and the type of information obtained from these studies.

The motivation for all this effort comes from both technological and fundamental scientific interest in the metal/silicon interface, which is especially important in the manufacture of electronic devices. The clean Si(100) surface shows a dominant 2x1 structure,¹ although some higher-order structures, such as c(4x2), p(2x2), c(2x2) and c(4x4), are also reported. The 2x1 reconstruction is generally believed to be due to the well-known Si dimer formation.² This surface is still chemically reactive since there is a dangling bond associated with each surface Si atom. Therefore, different atoms adsorbed on Si(100) will result in different structural and electronic property changes.

The chemical reactions of various metals with Si can be grouped as follows: (i) a very active chemical reaction which forms metal silicide at the interface such as Mo/Si and Ni/Si; (ii) passivation of the Si surface by forming a metal overlayer and removing the Si(100)2x1 reconstruction, e.g., As/Si and Sb/Si; (iii) medium interaction by adsorbing on specific sites of the Si surface and inducing more complex reconstruction; for example, In on Si can have (2x2) and (4x3) reconstructions depending on the temperature; (iv) less reactive so that the underlying Si substrate does not change upon metal adsorption, e.g., alkali metals on Si.

One of the most important characteristic features of the metal-Si interface is the nature of the potential barrier between the Fermi level in the metal and the majority carrier's band edge of the semiconductor - known as the Schottky barrier at that interface. This potential barrier is of central importance in determining the performance of Si devices. Since the chemisorption of metals on the Si surface is the early stage of the chemical reaction of metals with Si, their study is an important

Dist	Special
A-1	

first step to understand the mechanism of Schottky barrier formation, the bonding between metal and Si and the metal induced change of surface states.

II. Results

Our study on the metal/silicon interface for the last year has been focussed on the alkali metal (Na) and group V metals (As and Sb) on Si(100) surface. The main results are summarized below. As an appendix, we include a preprint of a paper we are about to submit entitled "*Ge(100) 2x1 and c(4x2) Surface Reconstructions Studied by ab-initio Total Energy Molecular Force Calculations*". This will indicate the nature and results of our study of the Ge(100) surface reconstructions. As a next step, we will study alkali metals adsorbed onto the Ge(100) surface.

A. Na adsorption on Si(100)2x1

We have studied Na chemisorption on the Si(100) surface.^{3,4} There are four possible adsorption sites on Si(100)(2x1), i.e. pedestal, cave, bridge and valley bridge sites and they are simulated by cluster models ranging from 22 to 77 atoms. A preliminary calculation excluded the bridge site because it has far lower adsorption energy than the other sites. For the remaining three sites, we calculated Na adsorption on both the unrelaxed silicon substrate and the relaxed substrate, since it is possible that surface relaxation might be of some relevance in the determination of the correct adsorption site. The calculated adsorption energy is shown in Table 1. When the substrate is unrelaxed, the cave site has the highest adsorption energy followed closely by the pedestal site with a difference of only 0.04~eV. It is hard to distinguish which is the most stable site with such a small energy difference. By taking into account the surface relaxation, one can see that the highest adsorption energy is now obtained for the cave site with a difference that is 0.17~eV higher than the pedestal site. On the other hand, the calculated bond lengths of Na-Si and Si-Si at cave site are the closest to the experimental results among the three sites. Thus, the cave site is the most favorable adsorption site for Na.

Table 1: Na adsorption energies (in eV) for the cave, pedestal and valley bridge sites in the cases of unrelaxed and relaxed Si(100)2x1 substrate.

	<u>unrelaxed</u>	<u>relaxed</u>
Cave	2.03	2.22
Pedestal	1.99	2.05
Valley-Bridge	1.72	1.92

As to the nature of the bonding between Na and Si, we found it is a mixture of ionic and covalent bonding. When compared with other groups of metal on Si(100), Na forms relatively weak bonding with Si. Because of this weak bonding, the Si(100)2x1 reconstruction remains unchanged when Na adsorbs on the surface.

B. Group V Metals on Si(100)

We first determined the optimal adsorption site of a single As or Sb atom on Si(100)1x1 and Si(100)2x1.^{5,6} There are four possible adsorption sites for each surface, and they are simulated by 8 clusters having 22 to 26 atoms. For As and Sb on Si(100)2x1, the bridge site has the highest adsorption energy and therefore is the most stable site among the four possible sites studied. For As and Sb on Si(100)1x1, we have different results which show that As prefers to adsorb on the bridge site and Sb on the hollow site. One does not expect such a result because, experimentally, As and Sb shows similar behaviour on the Si(100) surface. This discrepancy is resolved when metal-metal interactions are included in the calculation. To do that, we chose another set of larger clusters and put two metal atoms on several sites and in two different orientations with respect to the Si dimer on the clean Si(100)2x1 surface. The calculated results show that the bridge site has the highest adsorption energy for both As and Sb. The final results of our structural model are shown in Table 2 together with the experimental values. There is a quite good agreement between our theoretical results and experiment.

In the meantime, we found that As and Sb adsorbed on the Si(100) surface induce large unbalanced forces in the substrate because of the strong covalent bonding between metal and Si. This lead us to study the metal-induced passivation of Si(100)2x1. The study was conducted on a Sb₃Si₂₇H₃₂ cluster which includes a combination of two bridge sites and one cave site. If we put two metal atoms on the bridge site and one atom on the cave, we found a strong force in the substrate that tends break the Si dimer. Indeed, breaking the Si dimer would gain an extra 0.52~eV/dimer. The result is that the Si(100)2x1 reconstruction is removed by the adsorption of As or Sb atoms.

Table 2: Optimized structural parameters for As and Sb dimers on Si(100)(1x1) calculated from a 63 atom cluster model: h is the vertical height of the metal atom from the Si surface, and d_{As-Si} and d_{Sb-Si} stand for the closest distances between the metal and Si atom; distances between two As or Sb atoms are represented by d_{As-As} and d_{Sb-Sb} . All distances are in unit of Å.

		<u>Present</u>	<u>Theo.²</u>	<u>Exp.</u>
As/Si	h	1.43	1.41	1.26 ± 0.01^b , 1.43^b
	d_{As-Si}	2.45	2.44	-
	d_{As-As}	2.52	2.55	2.55 ± 0.01^c
Sb/Si	h	1.73	-	1.74 ± 0.05^d
	d_{Sb-Si}	2.61	-	2.63 ± 0.04^d
	d_{Sb-Sb}	2.93	-	2.88 ± 0.03^d

a Ref.[7]

b Ref.[8]

c Ref.[9]

d Ref.[10]

References

1. R.E. Schlier and H.E. Farnsworth, J. Chem. Phys. {Nbf 30}, 917 (1959).
2. D. Haneman, Rep. Prog. Phys. **50**, 1045 (1987) and references therein.
3. L. Spiess, P.S. Mangat, S.P. Tang, K.M. Schirm, A.J. Freeman and P. Soukiassian, Surf. Sci. Lett. (in press).
4. P.S. Mangat, P. Soukiassian, K.M. Schirm, Z. Hurych, L. Spiess, S.P. Tang, A.J. Freeman and B. Delley, Phys. Rev. B (in press).
5. S.P. Tang and A.J. Freeman, Phys. Rev. B **47**, 1460 (1993).
6. S.P. Tang and A.J. Freeman, Phys. Rev. B (Submitted).
7. R.I.G. Uhrberg, R.D. Bringans, R.Z. Bachrach and J.E. Northrup, Phys. Rev. Lett. **56**, 520 (1986).
8. J. Zegenhagen, J.R. Patel, B.M. Kincaid, J.A. Golovchenko, J.R. Mock, P.E. Freeland, R.J. Malik, and K.-G. Huang, Appl. Phys. Lett., **53**, 252 (1988).
9. N. Jedrecy, M. Sauvage-Simkin, R. Pinchaux, J. Massies, N. Greiser and V.H. Etgens, Surf. Sci. **230**, 197 (1990).
10. M.Richter, J.C.Woicik, J.Nogami, P.Pianetta, K.E. Miyano, A.A. Baski, T. Kendelewicz, C.E. Bouldin, W.E. Spicer, C.F. Quate, and I. Lindau, Phys. Rev. Lett. **65**, 3417 (1990).

A.J. FREEMAN
PUBLICATION LIST FOR ONR GRANT NO. N00014-89J-1290

a. PAPERS SUBMITTED TO REFEREED JOURNALS (AND NOT YET PUBLISHED)

None

b. PAPERS PUBLISHED IN REFEREED JOURNALS (14)

"Metal-metal Interfacial Bonding: Monolayer c(2x2) Cu on a Pt(001) Surface", (with T. Kramer, R. Podloucky, A. Neckel and H. Erschbaumer), *Surf. Sci.* **247** (1991) 58-68.

"Electronic Structure and Properties of $\text{YBa}_2\text{Cu}_4\text{O}_8$ ", (with Jaejun Yu and Key-Taeck Park), *Physica C* **172** (1991) 467-476.

"Electronic Structure Theory of Magnetism of Surfaces, Interfaces, and Overlayers", (with Chun Li), *Physica Scripta*, **T35** (1991) 172-176.

"Origin of Electric Field Gradients in High Temperature Superconductors: $\text{YBa}_2\text{Cu}_3\text{O}_7$ ", (with Jaejun Yu, R. Podloucky, P. Herzig, and P. Weinberger), *Phys. Rev. B* **43** (1991) 532.

"Noble and Alkali Metal Adsorption on the Silicon Surface", (with S. Tang, Ye Ling, S.H. Chou and B. Delley), in *Surface Physics and Related Topics - Festschrift for Prof. Xie Xide*, (World Scientific Co. Pte. Ltd., (1991), pp. 148-165.

"Electronic Structure Theory of Surface, Interface and Thin-film Magnetism", (with R. Wu), *J. Magn. Magn. Matls.* **100** (1991) 497-514.

"Determination of the Na/Si(100)2x1 Surface and Interface Geometry by Polarization-dependent Photoemission EXAFS and Ab-initio Total Energy Molecular Dmol Calculations", (with P.S. Mangat, P. Soukiassian, (with K.M. Schirm, Z. Hurych, L. Spiess, Shao-ping Tang and B. Delley, *Phys. Rev. B* **47**, 16 311 (1993).

"Sb Induced Passivation of the Si(100) Surface", (with Shaoping Tang), *Phys. Rev. B* **47** (1993) 1460.

"Combined Theoretical and Experimental Determination of the Atomic Structure and Adsorption Site of Na on Si(100) 2x1", (with L. Spiess, P.S. Mangat, S. Tang, K.M. Schirm and P. Soukiassian), *Surf. Sci. Lett.* **289** (1993) L631.

"Geometry and Mode Growth of Alkali Metal/Si(100)2x1 Interfaces", with P. Soukiassian, L.Spiess, K.M. Schirm, P.S. Mangat, J.A. Kubby and S.P. Tang), *J. Vac. Sci. Technol. B*, **11**, No. 4, Jul/Aug. 1993, p. 1431-1438.

Importance of Adsorbate-adsorbate Interactions for As and Sb Chemisorption on Si(100)", (with Shaoping Tang), *Phys. Rev. B* **48**, 8068 (1993).

"Sb Induced Passivation of the Si(100) Surface", (with Shaoping Tang), *Phys. Rev. B* **47**, 1460 (1993).

"Surface Properties of Si(111) 7x7 upon H and NH₃ Adsorption: A Local Density Functional Study", (with L. Ye and B. Delley), Phys. Rev. B **48**, 11 107 (1993).

"Ge(100) 2x1 and c(4x2) Surface Reconstructions Studied by *ab-initio* Total Energy Molecular Force Calculations", (with L. Spiess and P. Soukiasian), Phys. Rev. B **50**, 2249 (1994).

c. BOOKS (AND SECTIONS THEREOF) SUBMITTED FOR PUBLICATION (2)

"Electronic Structure Theory in the New Age of Computational Materials Science", Prefatory chapter for Ann. Rev. of Matls. Sci., Vol. 25, (1995) (to appear).

'Density Functional Theory as a Major Tool in Computational Materials Science", (with E. Wimmer), Ann. Rev. of Matls. Sci., Vol. 25, (1995) (to appear).

d. BOOKS (AND SECTIONS THEREOF) PUBLISHED (4)

"Local Density DMOL Studies of Noble and Alkali Metal Adsorption on the Silicon Surface", (with S. Tang, C.H. Chou, Ye Ling and B. Delley), in *Density Functional Methods in Chemistry*, Jan K. Labanowski and Jan W. Andzelm, eds., (Springer-Verlag New York, Inc., (1991)), pp. 61-75.

"Noble and Alkali Metal Adsorption on the Silicon Surface", (with S. Tang, Ye Ling, S.H. Chou and B. Delley), in *Surface Physics and Related Topics--Festschrift for Prof. Xie Xide*, (World Scientific Co. Pte. Ltd., 1991) pp. 148-165.

"Chemisorption and Catalytic Activity of Cu and Ag Atoms on Si(111) Surfaces", (with Shih-hung Chou, B. Delley, E. Wimmer, S. Grigoras, and T.M. Gentle), in *Surface Properties of Layered Structures*, series vol. in *Physics and Chemistry of Materials with Low Dimensional Structures*, F. Levy, ed., (Kluver Academic Publ. B.V., Inc. D. Reidel Publ. Co., Dordrecht, The Netherlands, 1990).

"Structural, Electronic and Magnetic Properties of Thin Films and Superlattices", (with A. Continenza and Chun Li), in *Materials Interfaces: Atomic-Level Structure and Properties*, D. Wolf and S. Yip, eds., Chapman and Hall Publ. (1992), pp. 275-298.

e. NUMBER OF PRINTED TECHNICAL REPORT & NON-REFEREED PAPERS (0)

f. NUMBER OF PATENTS FILED (0)

g. NUMBER OF PATENTS GRANTED (0)

h. NUMBER OF INVITED PRESENTATIONS AT WORKSHOPS OR PROFESSIONAL SOCIETY MEETINGS: (1)

"Structure and Electronic Properties of Complex Solids", Plenary lecture at 1992 Mtg. of 'Hauptversammlung der Deutschen Bunsen-Gesellschaft', Vienna, Austria, 28-30 May 1992.

i. CONTRIBUTED PRESENTATIONS AT TOPICAL OR SCENTIFIC/TECHNICAL SOCIETY CONFERENCES (7)

"LDF Total Energy and Atomic Force Study on C₆₀ X @ C₆₀, C₇₀ and the Interaction Between C₆₀ Molecules", (with L. Ye and B. Delley), 1992 APS Mtg., Indianapolis, IN, March 16-20, 1992.

"First Principles Study of the Surface Properties of Si(111)7x7 Upon H and NH₂ Adsorption", (with L. Ye and B. Delley), 1992 APS Mtg., Indianapolis, IN, March 16-20, 1992.

"Alkali Metal Adsorption on GaAs(110)", (with Shaoping Tang), 1992 APS Mtg., Indianapolis, IN, March 16-20, 1992.

"All-electron LDF Investigation of Clean and Cs Chemisorbed Si(001) 2x1 Surface", (with Laurent Spiess and Shaoping Tang), 1992 APS Mtg., Indianapolis, IN, March 16-20, 1992.

"Theoretical and Experimental Investigation of the Na/Si(100)2x1 Surface Structure", (with L. Spiess, Shao-Ping Tang, B. Delley, P.S. Mangat, K.M. Schirm, Z. Hurych and P. Soukiassian), Intl. Conf. on Solid Films and Surfaces (ICSF-6), Noisy-Le-Grand, France, June 30-July 3, 1992.

"Sb Induced Passivation of the Si(100) Surface", Shaoping Tang and A.J. Freeman, APS Mtg, Seattle, WA, March 22-26, 1993.

"First Principles DMol Cluster Calculations of the Ge(100) Surface", L. Spiess, A.J. Freeman and P. Soukiassian, ICFSI Conf. (1993).

j. HONORS/AWARDS/PRIZES FOR CONTRACT/GRANT EMPLOYEES:

Foreign Member of the Academy of Natural Sciences of Russia (2/92)

Foreign Member of the Russian Academy of Sciences - formerly the Soviet Academy of Sciences (1/93)

Foreign Member of the Polish Academy of Sciences (10/94)

k. TOTAL NUMBER OF GRADUATE STUDENTS AND POST-DOCS SUPPORTED AT LEAST 25%, THIS YEAR ON THIS CONTRACT/GRANT:

Grad Students (0) Post-docs (1)

How many of each are females or minorities? (0)